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(54) METHODS TO REJUVENATE A DEACTIVATED HYDROFORMYLATION CATALYST SOLUTION

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(58) **Field of Classification Search**
None
See application file for complete search history.

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(57) ABSTRACT

Disclosed herein are methods to rejuvenate a deactivated hydroformylation catalyst solution wherein the solution comprises rhodium, polyphosphoramidite ligands, and polyphosphoramidite ligand degradation products. In some embodiments, such methods comprise adding a peroxide to the deactivated hydroformylation catalyst solution.

8 Claims, No Drawings

METHODS TO REJUVENATE A DEACTIVATED HYDROFORMYLATION CATALYST SOLUTION

FIELD

The present disclosure relates generally to methods for rejuvenating deactivated hydroformylation catalyst solutions and in particular, to methods for rejuvenating deactivated hydroformylation catalyst solutions comprising polyphosphoramidite ligands.

BACKGROUND

Aldehydes can be prepared from olefins in a number of ways using hydroformylation. For example, olefins can be reacted with carbon monoxide and hydrogen in the presence of a polyphosphoramidite-modified rhodium catalyst to produce aldehydes containing three to twenty-one carbon atoms.

Although the root causes vary, a steady loss of catalyst activity over time is an issue with hydroformylation processes. For example, rhodium processes promoted by triphenylphosphine (TPP) are known to suffer intrinsic deactivation due to rhodium clustering and the formation of inhibitory phosphorous compounds (see, e.g., U.S. Pat. Nos. 4,277,627 and 4,605,780). Likewise, rhodium-bisphophite catalysts are inhibited by phosphorous-containing degradation products as detailed in U.S. Pat. No. 5,874,640. Thus, discovering and employing an effective strategy to mitigate catalyst deactivation is an important aspect of hydroformylation process development.

Rhodium-polyphosphoramidites are another type of hydroformylation catalyst where deactivation is an issue. There exists a need for a facile means to restore activity to a deactivated rhodium-polyphosphoamidite hydroformylation catalyst.

SUMMARY

Disclosed in embodiments herein are methods to rejuvenate deactivated hydroformylation catalyst solutions.

In one embodiment, the present invention relates to a method to rejuvenate a deactivated hydroformylation catalyst solution comprising rhodium, a polyphosphoramidite ligand, and polyphosphoramidite ligand degradation products, the method comprising adding a peroxide to the deactivated hydroformylation catalyst solution. In some embodiments, additional polyphosphoramidite ligand can be added to the catalyst solution after the addition of peroxide.

These and other embodiments are described in more detail in the Detailed Description.

DETAILED DESCRIPTION

The methods disclosed herein are particularly suitable for use in hydroformylation processes utiliting polyphosphoramidite ligands as part of the catalyst. Such hydroformylation processes comprise contacting CO, H_2, and at least one olefin under hydroformylation conditions sufficient to form at least one aldehyde product in the presence of a catalyst comprising, as components, a transition metal and a polyphosphoramidite ligand.

All references to the Periodic Table of the Elements and the various groups therein are to the version published in the CRC Handbook of Chemistry and Physics, 72nd Ed. (1991-1992) CRC Press, at page I-11.

Unless stated to the contrary, or implicit from the context, all parts and percentages are based on weight and all test methods are current as of the filing date of this application. For purposes of United States patent practice, the contents of any referenced patent, patent application or publication are incorporated by reference in their entirety (or its equivalent U.S. version is so incorporated by reference) especially with respect to the disclosure of definitions (to the extent not inconsistent with any definitions specifically provided in this disclosure) and general knowledge in the art.

As used herein, “a”, “an”, “the”, “at least one”, and “one or more” are used interchangeably. The terms “comprises”, “includes”, and variations thereof do not have a limiting meaning where these terms appear in the description and claims. Thus, for example, an aqueous composition that includes particles of “a” hydrophobic polymer can be interpreted to mean that the composition includes particles of “one or more” hydrophobic polymers.

Also herein, the recitations of numerical ranges by endpoints include all numbers subsumed in that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.). For the purposes of the invention, it is to be understood, consistent with what one of ordinary skill in the art would understand, that a numerical range is intended to include and support all possible subranges that are included in that range. For example, the range from 1 to 100 is intended to convey from 1.01 to 100, from 1 to 99.99, from 1.01 to 99.99, from 40 to 60, from 1 to 55, etc. Also herein, the recitations of numerical ranges and/or numerical values, including such recitations in the claims, can be read to include the term “about.” In such instances the term “about” refers to numerical ranges and/or numerical values that are substantially the same as those recited herein.

As used herein, the term “ppmw” means parts per million by weight.

For purposes of this invention, the term “hydrocarbon” is contemplated to include all permissible compounds having at least one hydrogen and one carbon atom. Such permissible compounds may also have one or more heteroatoms. In a broad aspect, the permissible hydrocarbons include acyclic (with or without heteroatoms) and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic organic compounds that can be substituted or unsubstituted.

As used herein, the term “substituted” is contemplated to include all permissible substituents of organic compounds unless otherwise indicated. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, alkyl, alkyloxy, aryl, aryloxy, hydroxyalkyl, aminoalkyl, in which the number of carbons can range from 1 to 20 or more, preferably from 1 to 12, as well as hydroxy, halo, and amino The permissible substituents can be one or more and the same or different for appropriate organic compounds. This invention is not intended to be limited in any manner by the permissible substituents of organic compounds.

As used herein, the term “hydroformylation” is contemplated to include, but not limited to, all permissible asymmetric and non-asymmetric hydroformylation processes that involve converting one or more substituted or unsubstituted olefinic compounds or a reaction mixture comprising one or more substituted or unsubstituted olefinic compounds to one or more substituted or unsubstituted aldehydes or a reaction mixture comprising one or more substituted or unsubstituted aldehydes.

The terms “reaction fluid”, “reaction medium”, “process fluid”, and “catalyst solution” are used interchangeably herein, and may include, but are not limited to, a mixture comprising: (a) a metal-polyphosphoramidite ligand complex catalyst, (b) free polyphosphoramidite ligand, (c) aldehyde product formed in the reaction, (d) unreacted reactants, (e) a solvent for said metal-polyphosphoramidite ligand complex catalyst and said free polyphosphoramidite ligand, and, optionally, (f) one or more phosphorus acidic compounds formed in the reaction (which may be homogeneous or heterogeneous, and these compounds include those adhered to process equipment surfaces) and (g) polyphosphoramidite ligand decomposition products such as the corresponding oxide. The reaction fluid can encompass, but is not limited to, (a) a fluid in a reaction zone, (b) a fluid stream on its way to a separation zone, (c) a fluid in a separation zone, (d) a recycle stream, (e) a fluid withdrawn from a reaction zone or separation zone, (f) a withdrawn fluid being treated with an aqueous buffer solution, (g) a treated fluid returned to a reaction zone or separation zone, (h) a fluid in an external cooler, and (i) ligand decomposition products and their salts.

The terms “ligand decomposition products” and “ligand degradation products” are used interchangeably herein and are contemplated to include, but not be limited to, small phosphorous compounds produced by rhodium-catalyzed side reactions of the parent ligand, as well as partially oxidized polyphosphoramidite.

Disclosed herein are methods to rejuvenate a deactivated hydroformylation catalyst solution wherein the solution comprises rhodium, polyphosphoramidite ligands, and polyphosphoramidite ligand degradation products. In some embodiments, such methods comprise adding a peroxide to the deactivated hydroformylation catalyst solution. In some embodiments, additional polyphosphoramidite ligand is added to the catalyst solution after the addition of peroxide.

The terms “aldehyde product”, “desired aldehyde product”, “product aldehyde” and “product aldehyde(s)” are used interchangeably and are contemplated to include the aldehyde(s) produced on-purpose from the hydroformylation reaction. Examples of such product aldehydes include propionaldehyde (produced from ethylene), butyraldehyde (produced from propylene) and valeraldehyde (produced from 1-butene or mixed butenes). In some embodiments, the deactivated hydroformylation catalyst solution further comprises at least one product aldehyde. In some such embodiments, a majority of the product aldehyde can be removed prior to adding the peroxide. The product aldehyde can be removed, in some embodiments by vaporization.

In some embodiments, the deactivated hydroformylation catalyst solution is at ambient temperature when the peroxide is added. In some embodiments, the temperature of the deactivated hydroformylation catalyst solution is between 0° C. and 40° C. when the peroxide is added. In some embodiments, the deactivated hydroformylation catalyst solution is at a temperature of 70° C. or greater when the peroxide is added. The deactivated hydroformylation catalyst solution is at a temperature of 100° C. or greater when the peroxide is added in some embodiments.

The peroxide, in some embodiments, comprises hydrogen peroxide, peroxy esters, peroxydicarbonates, dialkyl peroxides, hydroperoxides, peroxyketals, or a combination thereof.

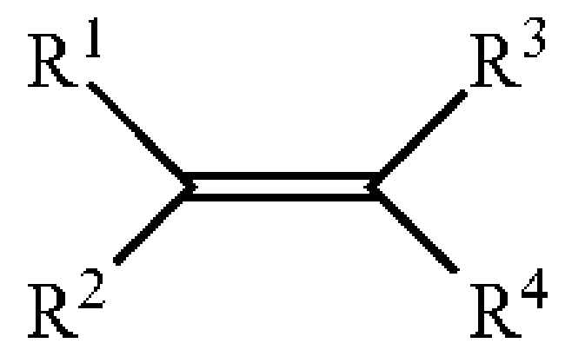
Hydrogen and carbon monoxide may be obtained from any suitable source, including petroleum cracking and refinery operations. Syngas mixtures are a preferred source of hydrogen and CO.

Syngas (from synthesis gas) is the name given to a gas mixture that contains varying amounts of CO and H_2. Production methods are well known. Hydrogen and CO typically are the main components of syngas, but syngas may contain CO_2 and inert gases such as N_2 and Ar. The molar ratio of H_2 to CO varies greatly but generally ranges from 1:100 to 100:1 and preferably between 1:10 and 10:1. Syngas is commercially available and is often used as a fuel source or as an intermediate for the production of other chemicals. The most preferred H_2:CO molar ratio for chemical production is between 3:1 and 1:3 and usually is targeted to be between about 1:2 and 2:1 for most hydroformylation applications.

As used herein, “peroxides” include hydrogen peroxide, organic peroxides, and mixtures thereof. Peroxides are contemplated to comprise hydrogen peroxide, as well as organic compounds containing at least one peroxide group (ROOR') wherein at least one of R and R'comprises a carbon atom. Illustrative families and organic peroxide compounds include peroxy esters (e.g. t-butylperbenzoate), peroxydicarbonates (e.g. di-2-ethylhexyl peroxydicarbonate), dialkyl peroxides (e.g. di-t-butyl peroxides), hydroperoxides (e.g. t-butyl hydroperoxide) and peroxyketals (e.g.1,1'di(t-butyl peroxy)-3,3,5-trimethylcyclohexane).

The substituted or unsubstituted olefinic unsaturated reactants that may be employed in the hydroformylation process include both optically active (prochiral and chiral) and non-optically active (achiral) olefinic unsaturated compounds containing from 2 to 40, preferably 3 to 20, carbon atoms. These compounds are described in detail in U.S. Pat. No. 7,863,487. Such olefinic unsaturated compounds can be terminally or internally unsaturated and be of straight-chain, branched chain or cyclic structures, as well as olefin mixtures, such as obtained from the oligomerization of propene, butene, isobutene, etc. (such as so called dimeric, trimeric or tetrameric propylene and the like, as disclosed, for example, in U.S. Pat. Nos. 4,518,809 and 4,528,403.

Prochiral and chiral olefins useful in the asymmetric hydroformylation that can be employed to produce enantiomeric aldehyde mixtures include those represented by the formula:



wherein R^1, R^2, R^3 and R^4 are the same or different (provided that R^1 is different from R^2 or R^3 is different from R^4) and are selected from hydrogen; alkyl; substituted alkyl, said substitution being selected from dialkylamino such as benzylamino and dibenzylamino, alkoxy such as methoxy and ethoxy, acyloxy such as acetoxy, halo, nitro, nitrile, thio, carbonyl, carboxamide, carboxaldehyde, carboxyl, and carboxylic ester; aryl including phenyl; substituted aryl including phenyl, said substitution being selected from alkyl, amino including alkylamino and dialkylamino such as benzylamino and dibenzylamino, hydroxy, alkoxy such as methoxy and ethoxy, acyloxy such as acetoxy, halo, nitrile, nitro, carboxyl, carboxaldehyde, carboxylic ester, carbonyl, and thio; acyloxy such as acetoxy; alkoxy such as methoxy and ethoxy; amino including alkylamino and dialkylamino such as benzylamino and dibenzylamino; acylamino and diacylamino such as acetylbenzylamino and diacetylamino; nitro; carbonyl; nitrile; carboxyl; carboxamide; carboxaldehyde; carboxylic ester; and alkylmercapto such as methylmercapto. It is understood that the prochiral and chiral olefins of this definition also include molecules of the above general formula where the R groups are connected to form ring compounds, e.g., 3-methyl-1-cyclohexene, and the like.

Illustrative optically active or prochiral olefinic compounds useful in asymmetric hydroformylation are described, for example, in U.S. Pat. Nos. 4,329,507, 5,360,938 and 5,491,266.

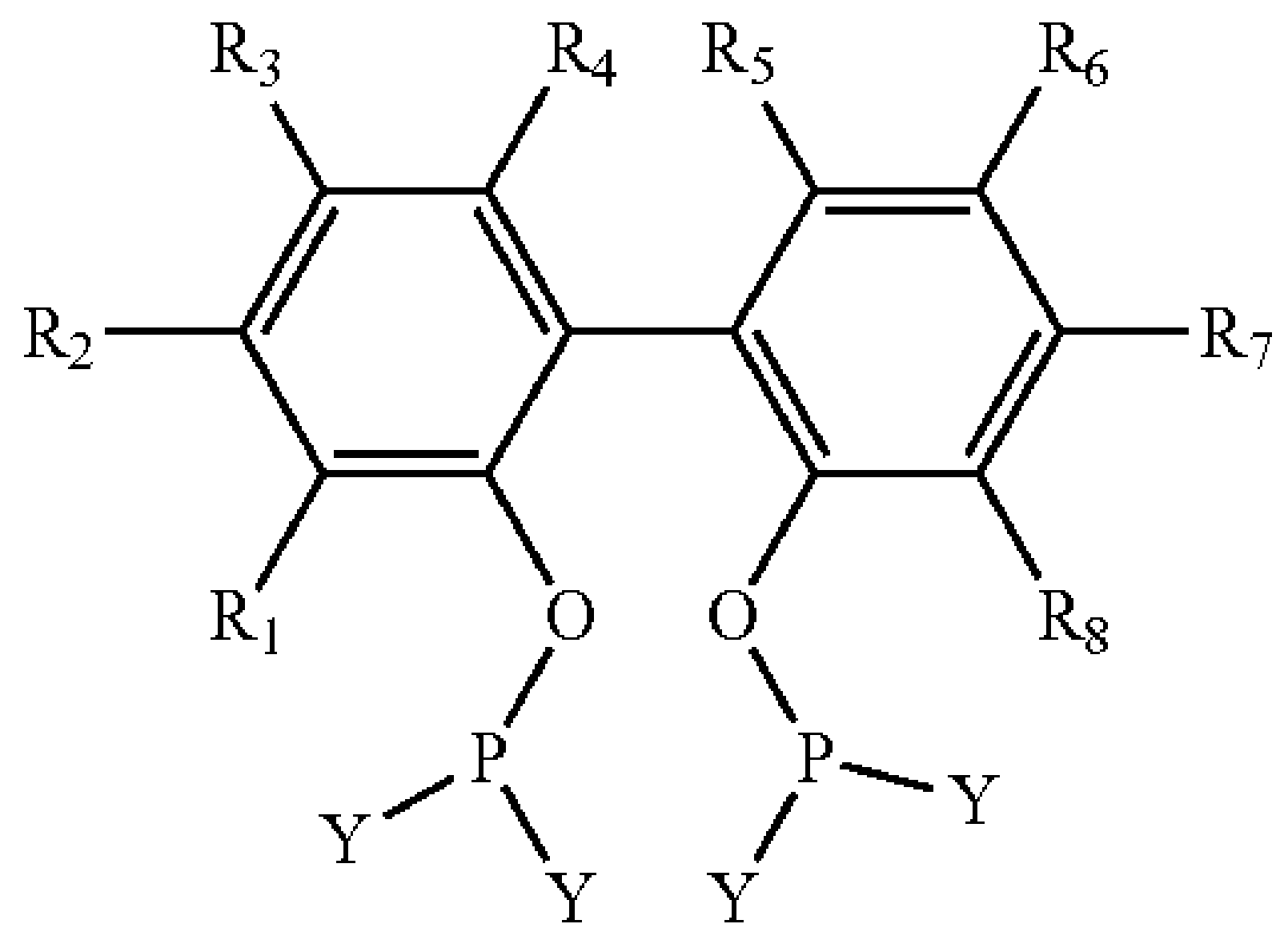
A solvent advantageously is employed in the hydroformylation process. Any suitable solvent that does not unduly interfere with the hydroformylation process can be used. By way of illustration, suitable solvents for rhodium catalyzed hydroformylation processes include those disclosed, for example, in U.S. Pat. Nos. 3,527,809; 4,148,830; 5,312,996; and 5,929,289. Non-limiting examples of suitable solvents include saturated hydrocarbons (alkanes), aromatic hydrocarbons, water, ethers, aldehydes, ketones, nitriles, alcohols, esters, and aldehyde condensation products. Specific examples of solvents include: tetraglyme, pentanes, cyclohexane, heptanes, benzene, xylene, toluene, diethyl ether, tetrahydrofuran, butyraldehyde, and benzonitrile. The organic solvent may also contain dissolved water up to the saturation limit. Illustrative preferred solvents include ketones (e.g. acetone and methylethyl ketone), esters (e.g. ethyl acetate, di-2-ethylhexyl phthalate, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate), hydrocarbons (e.g. toluene), nitrohydrocarbons (e.g., nitrobenzene), ethers (e.g., tetrahydrofuran (THF)) and sulfolane. In rhodium catalyzed hydroformylation processes, it may be preferred to employ, as a primary solvent, aldehyde compounds corresponding to the aldehyde products desired to be produced and/or higher boiling aldehyde liquid condensation by-products, for example, as might be produced in situ during the hydroformylation process, as described for example in U.S. Pat. Nos. 4,148,830 and 4,247,486. The primary solvent will normally eventually comprise both aldehyde products and higher boiling aldehyde liquid condensation by-products ("heavies"), due to the nature of the continuous process. The amount of solvent is not especially critical and need only be sufficient to provide the reaction medium with the desired amount of transition metal concentration. Typically, the amount of solvent ranges from about 5 percent to about 95 percent by weight, based on the total weight of the reaction fluid. Mixtures of solvents may be employed.

In general, metal-polyphosphoramidite catalysts may be preformed or formed in situ and comprise a metal precursor in combination with a polyphosphoramidite ligand, carbon monoxide and optionally hydrogen. The catalyst complex may be present in mononuclear, dinuclear and/or higher nuclearity forms. However, the exact structure of the catalyst is not known.

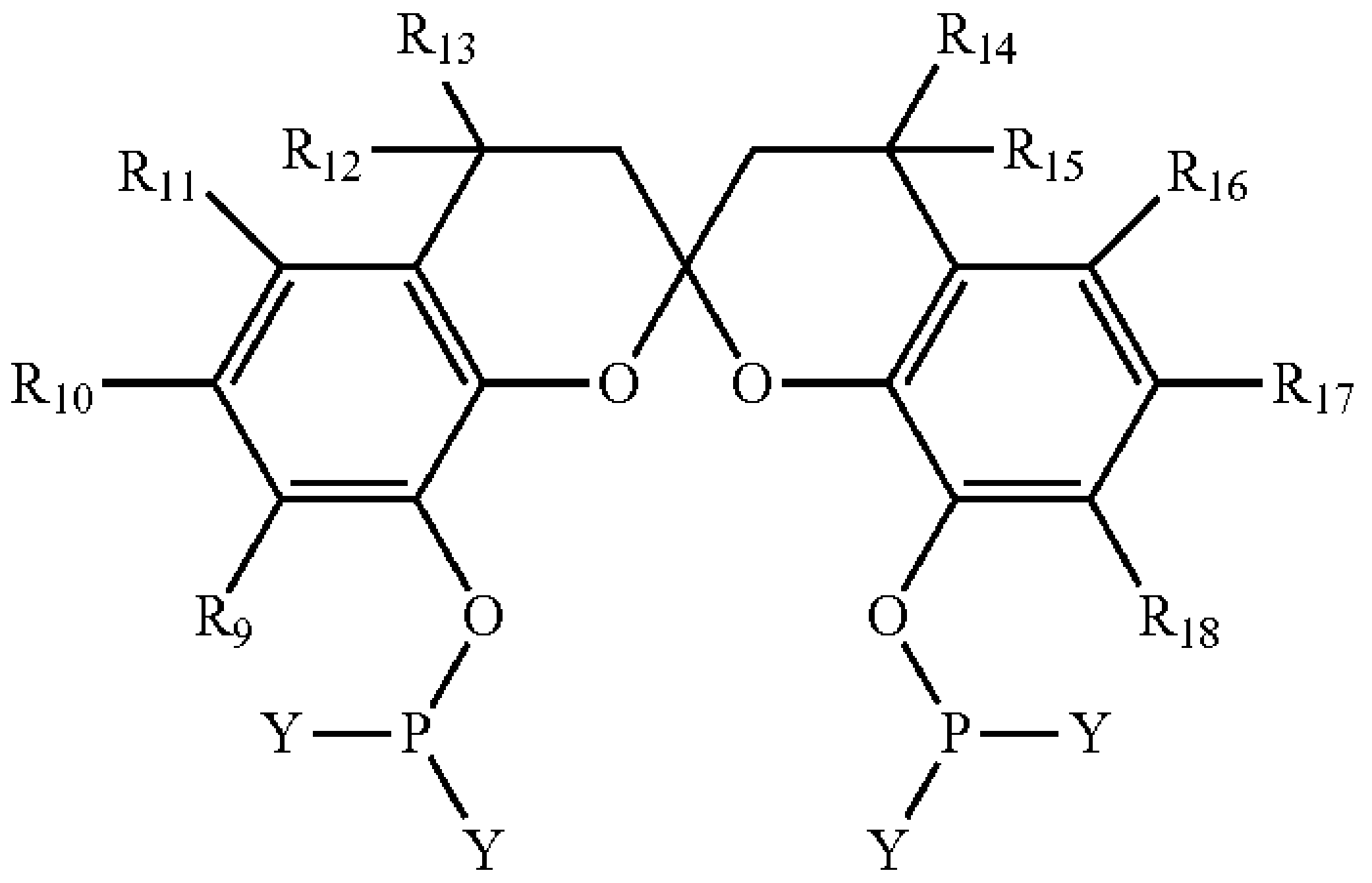
The metal-polyphosphoramidite ligand complex catalyst can be optically active or non-optically active. The metals can include Group 8, 9 and 10 metals selected from rhodium (Rh), cobalt (Co), iridium (Ir), ruthenium (Ru), iron (Fe), nickel (Ni), palladium (Pd), platinum (Pt), osmium (Os) and mixtures thereof, with the preferred metals being rhodium, cobalt, iridium and ruthenium, more preferably rhodium, cobalt and ruthenium, especially rhodium. Mixtures of these metals may be used. The permissible polyphosphoramidite ligands that make up the metal-polyphosphoramidite ligand complexes and free polyphosphoramidite ligand include tri-, tetra-, and higher polyorganophosphorus compounds. Mixtures of ligands may be employed in the metal-polyphosphoramidite ligand complex catalyst and/or free ligand, and such mixtures may be the same or different.

The polyphosphoramidite ligands that may serve as the ligand of the invention may be comprised of Formula I, II III, or IV:

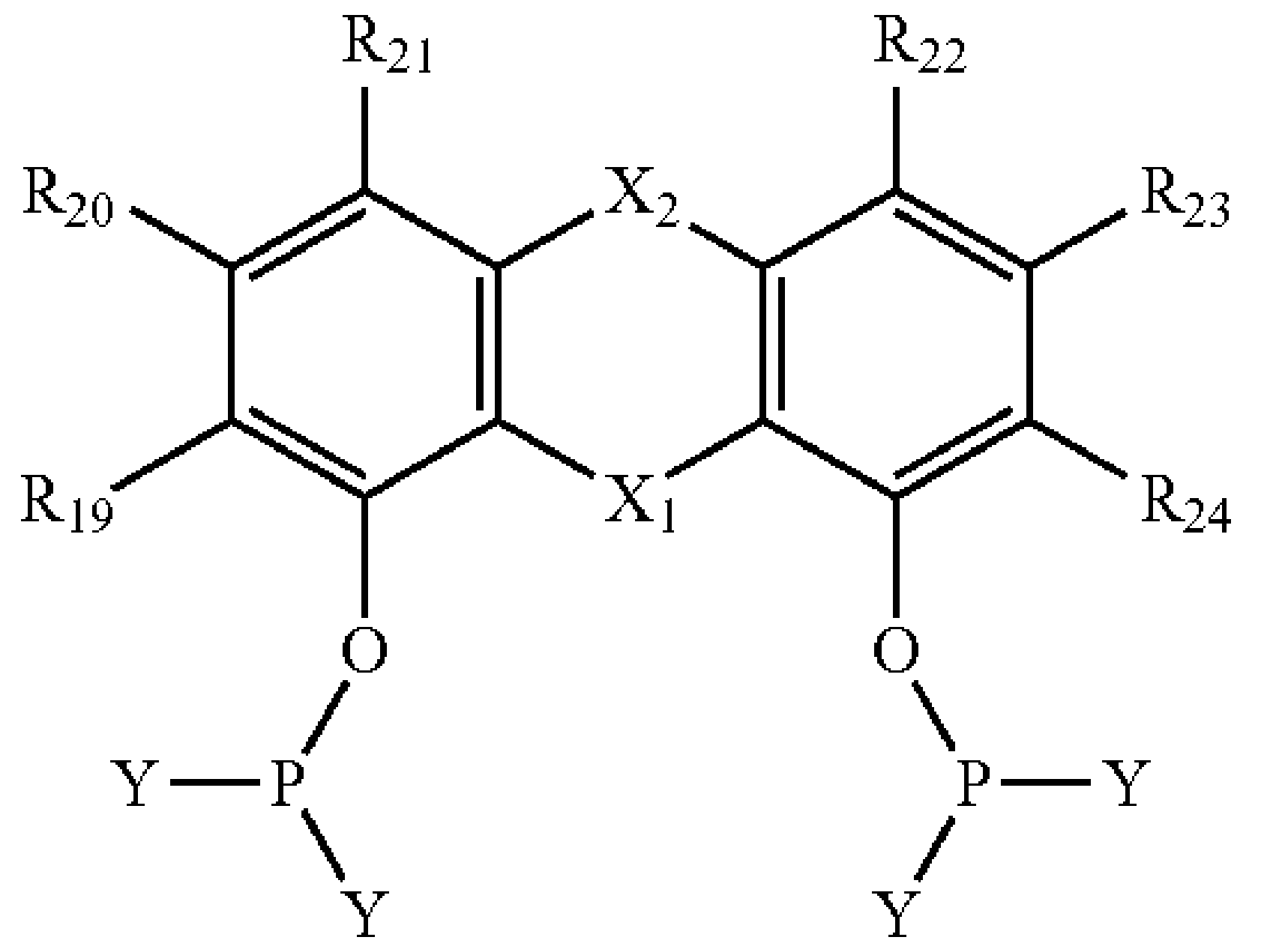
Formula I



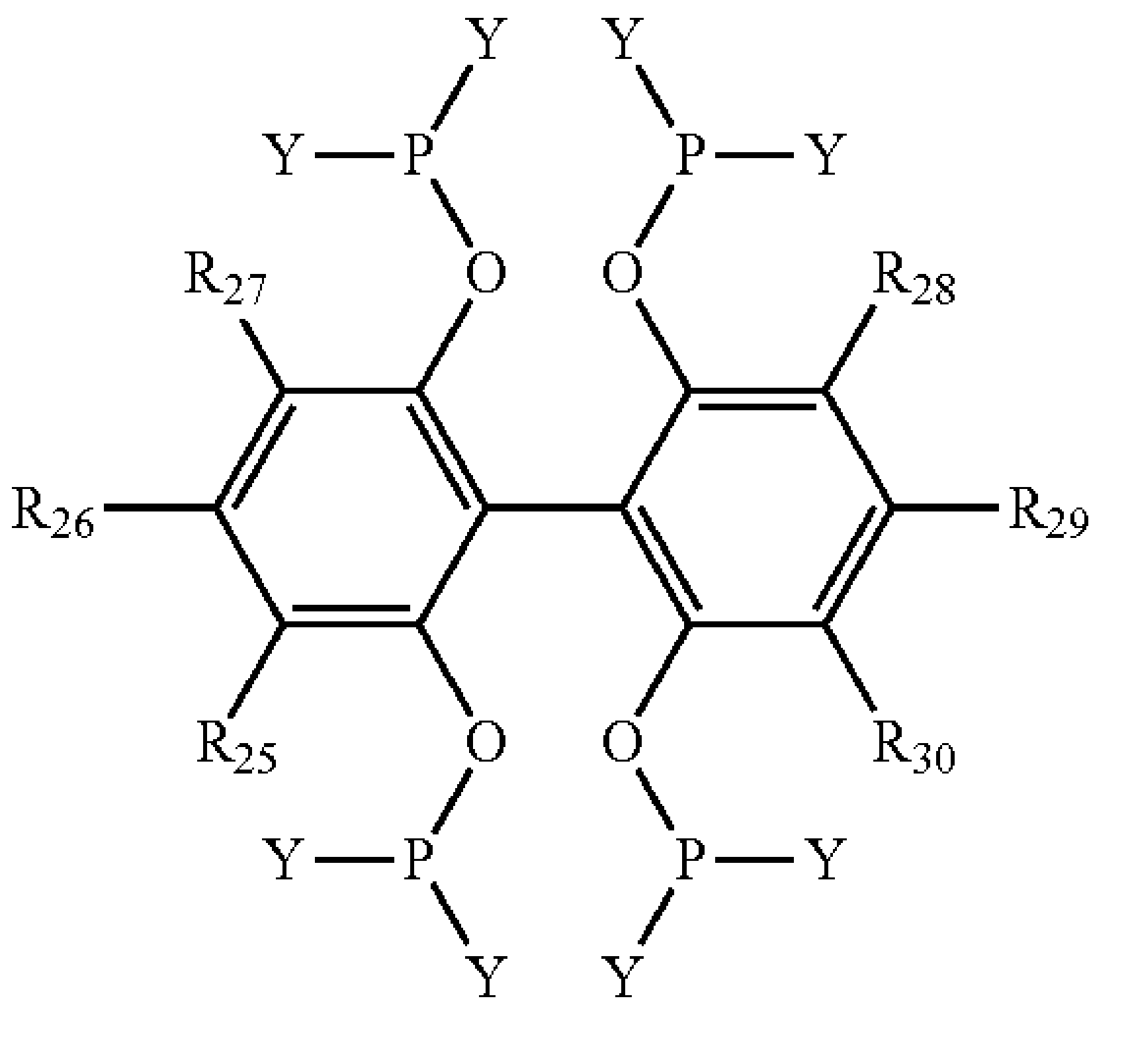
Formula II



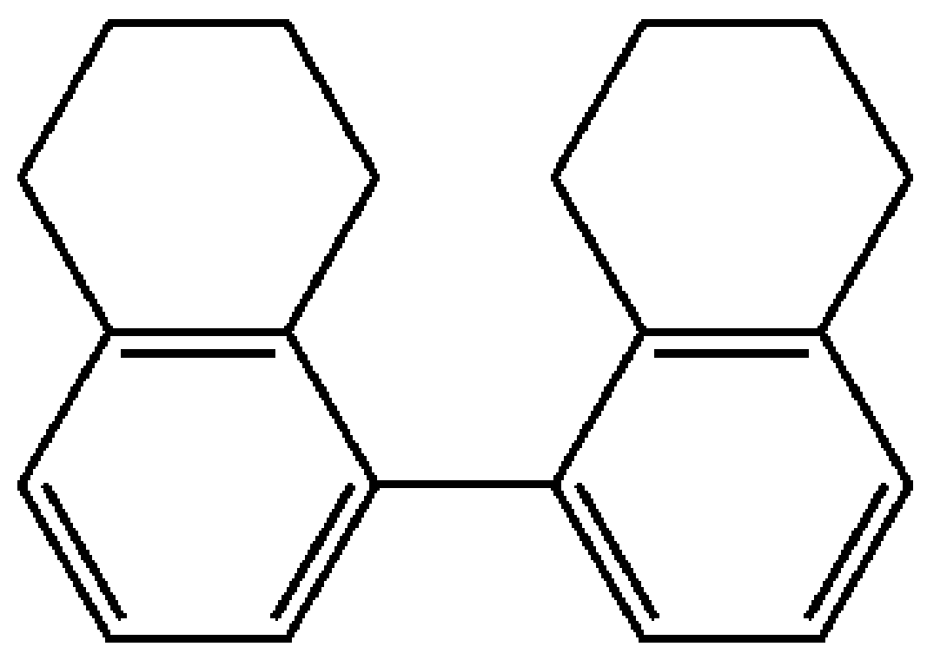
Formula III



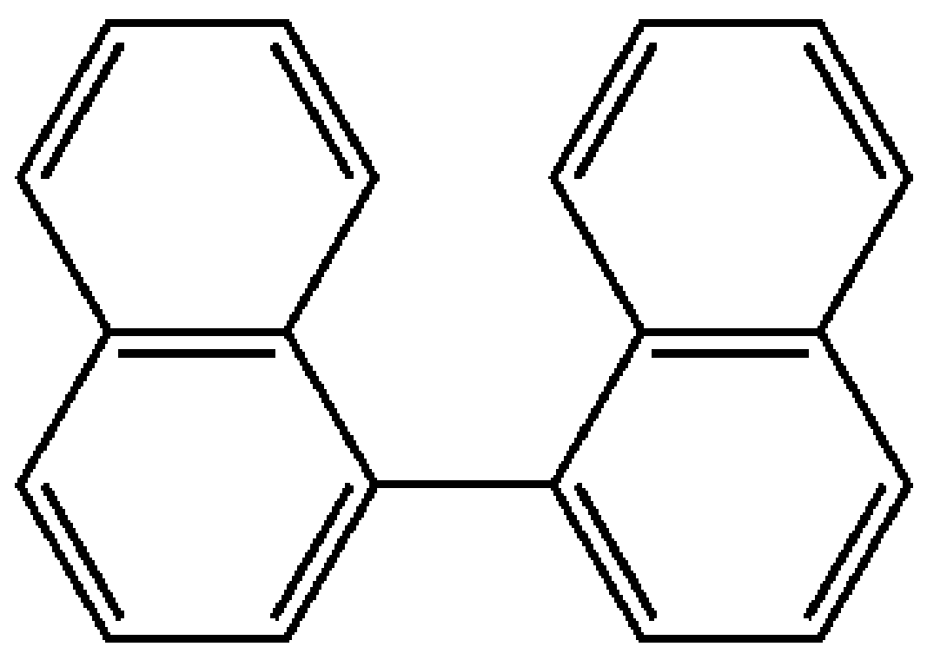
Formula IV



in which each O and P are oxygen and phosphorous atoms respectively; each R_1-R_{30} are independently a hydrogen, a hydrocarbyl group, an aromatic ring, a heteroaromatic ring or a halogen atom, or a heterocarbyl group selected from the groups consisting of NR_2, OR and SR, where R is a hydrocarbyl group of C1 to C20, or heterohydrocarbyl group having 1 to 20 atoms, each independently selected from C or a heteroatom, wherein each heteroatom is independently O, S, Si, Ge, P, or N, and may themselves be substituted or unsubstituted as required by the valency of the heteroatom. R_1 to R_{24} may optionally comprise cycloalkyl or aryl groups fused to the biaryl moiety such as:



or

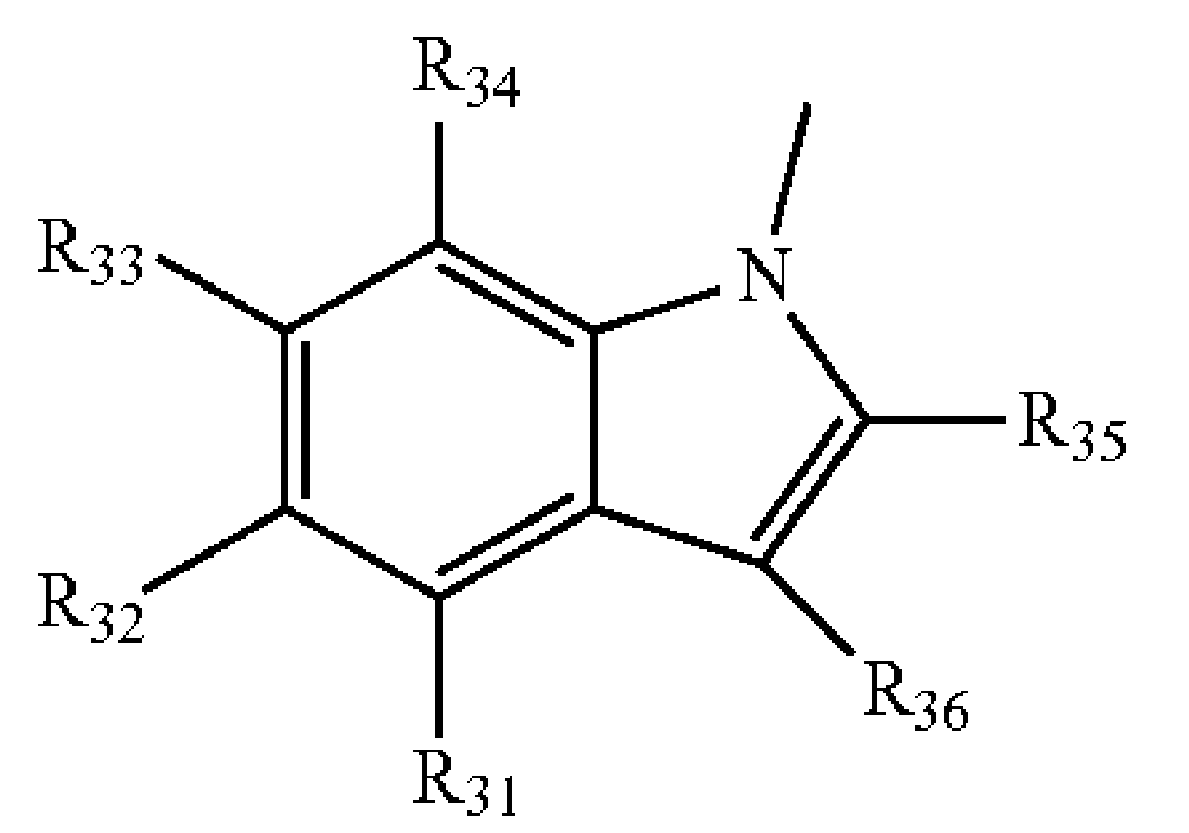


For Formula I, II, III, or IV, each aryl, heteroaryl, hydrocarbyl, heterohydrocarbyl, hydrocarbylene, and heterohydrocarbylene group independently is unsubstituted or substituted with one or more substituents R^v. Each R^v independently is a halogen atom, polyfluoroalkyl substitution, unsubstituted C1 to C18 alkyl, F_3C—, FCH_2O—, F_2HCO—, F_3CO—, R_3Si, R_3Ge, RO, RS, RS(O), $RS(O)_2$, R_2P, R_2N, $R_2C{=}N$, NC, RC(O)O, ROC(O), RC(O)N(R), or $R_2NC(O)$, or two of the R^v are taken together to form an un unsubstituted C1 to C18 alkylene, wherein each R independently is an unsubstituted C1 to C18 alkyl. Optionally, two of the R^v are taken together to form a ring, where the ring can be cyclic or polycyclic.

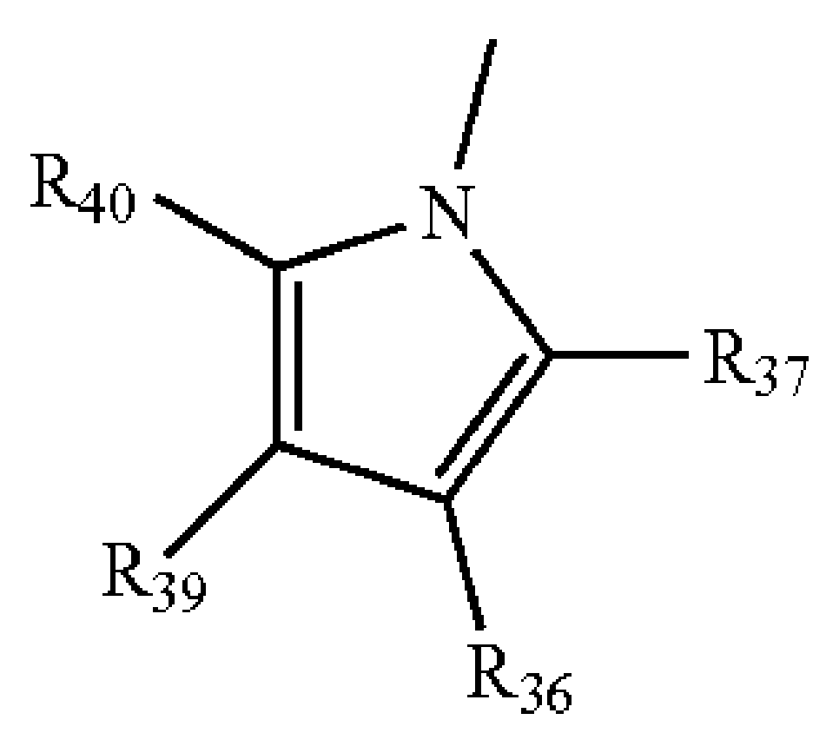
For Formula III, X_1 is CH_2 or O, while X_2 is O or $C(R_{25})_2$, and each R_{25} may be the same or different and is a hydrogen, a cycloaliphatic group, an aromatic ring, a heteroaromatic ring or a halogen atom, or a heterocarbyl group selected from the groups consisting of NR_2, OR and SR, where R is a hydrocarbyl group of C_1 to C_{20}, or heterohydrocarbyl group having 1 to 20 atoms, each independently selected from C or a heteroatom, wherein each heteroatom is independently O, S, Si, Ge, P, or N, and may themselves be substituted or unsubstituted as required by the valency of the heteroatom. Two R_{25} groups may combine in a fused ring. Y is a an aromatic ring or a heteroaromatic ring, and may be substituted or unsubstituted.

In some embodiments, instead of including both X_1 and X_2, Formula III may include only one of X_1 and X_2, but not both. In such embodiments, when only one of X_1 or X_2 is present, the carbon valences are satisfied by hydrogen.

Each Y is the same or different and is an indolyl or pyrrolyl group bound via the nitrogen atom to phosphorus, such as:



or



where each of R_{31}-R_{40} are the same or different and may be a hydrogen, a hydrocarbyl group, an aromatic ring, a heteroaromatic ring or a halogen atom.

In one embodiment, the metal-polyphosphoramidite catalyst is a composition comprising rhodium and at least one polyphosphoramidite ligand of Formula I, II, III or IV. In some embodiments, the catalyst rejuvenated using processes of the present invention comprises rhodium complexed with a polyphosphoramidite ligand; the rhodium complex may additionally contain any or all of olefin, hydrogen, and carbon monoxide. For example, the resting state of a catalyst may comprise the rhodium-ligand dicarbonyl hydride complex.

In absolute terms the rhodium concentration in the liquid body can range from about 25 ppm to about 1200 ppm of rhodium calculated as free metal. Analytical techniques for measuring rhodium concentration are well known to the skilled person, and include atomic absorption (AA), inductively coupled plasma (ICP) and X-ray fluorescence (XRF); AA is typically preferred. The polyphosphoramidite is present in the range of about 0.1 percent to about 1 percent by weight, based on the weight of the total reaction mixture, and in an amount sufficient to provide at least 0.1 moles of free polyphosphoramidite per mole of rhodium.

In general, the optimum catalyst concentration will depend on the olefin substrate employed. For example, it is well known that the hydroformylation rate for internal and branched internal olefins is slower than for linear alpha olefins, thus more catalyst will be required to achieve the desired conversion in those cases. For industrial processes, economic considerations require that the olefin conversion be as high as practical, thus engineering designs and process parameters—including catalyst concentration—must be adjusted accordingly.

The metal-polyphosphoramidite ligand complex catalysts may be in homogeneous or heterogeneous form. For instance, preformed rhodium hydrido-carbonyl-polyphosphoramidite ligand catalysts may be prepared and introduced into a hydroformylation reaction mixture. More preferably, the rhodium-polyphosphoramidite ligand complex catalysts can be derived from a rhodium catalyst precursor that may be introduced into the reaction medium for in situ formation of the active catalyst. For example, rhodium catalyst precursors such as rhodium dicarbonyl acetylacetonate, Rh_2O_3, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(NO_3)_3$ and the like may be introduced into the reaction mixture along with the polyphosphoramidite ligand for the in situ formation of the active catalyst. In a preferred embodiment, rhodium dicarbonyl acetylacetonate is employed as a rhodium precursor and reacted in the presence of a solvent with the polyphosphoramidite ligand to form a catalytic rhodium-polyphosphoramidite ligand complex precursor that is introduced into the reactor along with excess (free) polyphosphoramidite ligand for the in situ formation of the active catalyst. In any event, it is sufficient that carbon monoxide, hydrogen and the polyphosphoramidite ligand are all ligands that are capable of being complexed with the metal and that an active metal-polyphosphoramidite ligand catalyst is present in the reaction mixture under the conditions used in the hydroformylation reaction. Carbonyl, hydride, and polyphosphoramidite ligands may be complexed to the rhodium either prior to or in situ during the hydroformylation process.

The catalyst precursor composition can be prepared by forming a solution of rhodium dicarbonyl acetylacetonate, an organic solvent and a polyphosphoramidite ligand. The polyphosphoramidite ligand readily replaces at least one of the carbonyl ligands of the rhodium acetylacetonate complex precursor as witnessed by the evolution of carbon monoxide gas.

Accordingly, the metal-organophosphorus ligand complex catalyst advantageously comprise the metal complexed with carbon monoxide and a polyphosphoramidite ligand, said ligand being bonded (complexed) to the metal in a chelated and/or non-chelated fashion.

In addition to the metal-polyphosphoramidite ligand complex catalyst, free polyphosphoramidite ligand (i.e., ligand that is not complexed with the metal) may also be present in the reaction medium. The significance of free ligand is taught in U.S. Pat. No. 3,527,809, GB 1,338,225, and Brown et al., "Homogeneous Hydroformylation of Alkenes with

Hydridocarbonyltris(triphyenylphosphine)rhodium(I) as Catalyst," *Journal of the Chemical Society,* 1970, pages 2759 and 2761. The free polyphosphoramidite ligand may correspond to any of the above-defined polyphosphoramidite ligands discussed above. It is preferred that the free polyphosphoramidite ligand be the same as the polyphosphoramidite ligand of the metal-polyphosphoramidite ligand complex catalyst employed. However, such ligands need not be the same in any given process. The hydroformylation process of this invention may involve from 0.1 moles or less to 10 moles or higher of free polyphosphoramidite ligand per mole of metal in the reaction medium. In some embodiments, the hydroformylation process is carried out in the presence of from 1 to 5 moles of polyphosphoramidite ligand per mole of metal present in the reaction medium. In some embodiments, for polyphosphoramidite ligand, from 1 to 3 moles of polyphosphoramidite ligand are employed per mole of metal. Said amounts of polyphosphoramidite ligand are the sum of both the amount of polyphosphoramidite ligand that is bound (complexed) to the metal present and the amount of free polyphosphoramidite ligand present. If desired, additional polyphosphoramidite ligand can be supplied to the reaction medium of the hydroformylation process at any time and in any suitable manner, e.g. to maintain a predetermined level of free ligand in the reaction medium.

The hydroformylation process, and conditions for its operation, are well known. The hydroformylation processes may be asymmetric or non-asymmetric, the preferred processes being non-asymmetric, and may be conducted in any batch, continuous or semi-continuous fashion and may involve any catalyst liquid and/or gas recycle operation desired. Thus, it should be clear that the particular hydroformylation process for producing such aldehydes from an olefinic unsaturated compound, as well as the reaction conditions and ingredients of the hydroformylation process are not critical features of this invention other than the polyphosphoramide ligand employed in the process.

The recycle procedure generally involves withdrawing a portion of the liquid reaction medium containing the catalyst and aldehyde product from the hydroformylation reactor, i.e., reaction zone, either continuously or intermittently, and recovering the aldehyde product therefrom by use of a composite membrane, such as disclosed in U.S. Pat. Nos. 5,430,194 and 5,681,473, or by the more conventional and preferred method of distilling it, i.e. vaporization separation, in one or more stages under normal, reduced or elevated pressure, as appropriate, in a separate distillation zone, the non-volatilized metal catalyst containing residue being recycled to the reaction zone as disclosed, for example, in U.S. Pat. No. 5,288,918. Condensation of the volatilized materials, and separation and further recovery thereof, e.g., by further distillation, can be carried out in any conventional manner, the crude aldehyde product can be passed on for further purification and isomer separation, if desired, and any recovered reactants, e.g., olefinic starting material and syngas, can be recycled in any desired manner to the hydroformylation zone (reactor). The recovered metal catalyst containing raffinate of such membrane separation or recovered non-volatilized metal catalyst containing residue of such vaporization separation can be recycled, to the hydroformylation zone (reactor) in any conventional manner desired.

In one embodiment, the hydroformylation reaction fluid includes any fluid derived from any corresponding hydroformylation process that contains at least some amount of four different main ingredients or components, i.e., the aldehyde product, a metal-polyphosphoramidite ligand complex catalyst, free polyphosphoramidite ligand and a solvent for said catalyst and said free ligand. The hydroformylation reaction mixture compositions can and normally will contain additional ingredients such as those that have either been deliberately employed in the hydroformylation process or formed in situ during said process. Examples of such additional ingredients include unreacted olefin starting material, carbon monoxide and hydrogen gases, and in situ formed by-products, such as saturated hydrocarbons and/or unreacted isomerized olefins corresponding to the olefin starting materials, ligand degradation compounds, and high boiling liquid aldehyde condensation by-products, as well as other inert co-solvent type materials or hydrocarbon additives, if employed.

The reaction conditions of the hydroformylation process may include any suitable type hydroformylation conditions heretofore employed for producing optically active and/or non-optically active aldehydes. The hydroformylation reaction conditions employed will be governed by the type of aldehyde product desired. For instance, the total gas pressure of hydrogen, carbon monoxide and olefin starting compound of the hydroformylation process may range from 1 to 69,000 kPa. In general, however, it is preferred that the process be operated at a total gas pressure of hydrogen, carbon monoxide and olefin starting compound of less than 14,000 kPa and more preferably less than 3,400 kPa. The minimum total pressure is limited predominantly by the amount of reactants necessary to obtain a desired rate of reaction. More specifically, the carbon monoxide partial pressure of the hydroformylation process is preferably from 1 to 6,900 kPa, and more preferably from 21 to 5,500 kPa, while the hydrogen partial pressure is preferably from 34 to 3,400 kPa and more preferably from 69 to 2,100 kPa. In general, the molar ratio of gaseous H_2:CO may range from 1:10 to 100:1 or higher, the more preferred molar ratio being from 1:10 to 10:1.

In general, the hydroformylation process may be conducted at any operable reaction temperature. Advantageously, the hydroformylation process is conducted at a reaction temperature from −25° C. to 200° C., preferably from 50° C. to 120° C.

The hydroformylation process may be carried out using equipment and systems known to those of skill in the art. Examples of such equipment and systems can be found in U.S. Pat. Nos. 4,247,486, 5,105,018, 5,367,106, 6,642,420, 7,446,231, 8,389,774, 8,404,903 and 9,067,876, and in PCT Publication Nos. WO2015/047723, WO2015/094781, which are hereby incorporated by reference.

In one embodiment, the hydroformylation process useful in this invention may be carried out in a multistaged reactor such as described, for example, in U.S. Pat. No. 5,728,893. Such multistaged reactors can be designed with internal, physical barriers that create more than one theoretical reactive stage per vessel.

It is generally preferred to carry out the hydroformylation process in a continuous manner Continuous hydroformylation processes are well known in the art. The continuous process can be carried out in a single pass mode, i.e., wherein a vaporous mixture comprising unreacted olefinic starting material(s) and vaporized aldehyde product is removed from the liquid reaction mixture from whence the aldehyde product is recovered and make-up olefinic starting material(s), carbon monoxide and hydrogen are supplied to the liquid reaction medium for the next single pass through without recycling the unreacted olefinic starting material(s). Such types of recycle procedure are well known in the art and may involve the liquid recycling of the metal-polyphosphoramidite complex catalyst fluid separated from the desired aldehyde reaction product(s), such as disclosed, for example, in U.S. Pat. No. 4,148,830 or a gas recycle procedure such as disclosed, for example, in U.S. Pat. No. 4,247,486, as well as a combination of both a liquid and gas recycle procedure if desired. The most preferred hydroformylation process comprises a continuous liquid catalyst recycle process. Suitable liquid catalyst recycle procedures are disclosed, for example, in U.S. Pat. Nos. 4,668,651; 4,774,361; 5,102,505 and 5,110,990.

In one embodiment, the aldehyde product mixtures may be separated from the other components of the crude reaction mixtures in which the aldehyde mixtures are produced by any suitable method such as, for example, solvent extraction, crystallization, distillation, vaporization, wiped film evaporation, falling film evaporation, phase separation, filtration, or any combination thereof. It may be desired to remove the aldehyde products from the crude reaction mixture as they are formed through the use of trapping agents as described in WO 88/08835. One method for separating the aldehyde mixtures from the other components of the crude reaction mixtures is by membrane separation, which is described, for example in U.S. Pat. Nos. 5,430,194 and 5,681,473.

As indicated above, the desired aldehyde product may be recovered from the reaction mixtures. For example, the recovery techniques disclosed in U.S. Pat. Nos. 4,148,830 and 4,247,486 can be used. For instance, in a continuous liquid catalyst recycle process the portion of the liquid reaction mixture (containing aldehyde product, catalyst, etc.), i.e., reaction fluid, removed from the reaction zone can be passed to a separation zone, e.g., vaporizer/separator, wherein the desired aldehyde product can be separated via distillation, in one or more stages, under normal, reduced or elevated pressure, from the liquid reaction fluid, condensed and collected in a product receiver, and further purified if desired. The remaining non-volatilized catalyst containing liquid reaction mixture may then be recycled back to the reactor as may if desired any other volatile materials, e.g., unreacted olefin, together with any hydrogen and carbon monoxide dissolved in the liquid reaction after separation thereof from the condensed aldehyde product, e.g., by distillation in any conventional manner In general, it is preferred to separate the desired aldehyde product from the catalyst-containing reaction mixture under reduced pressure and at low temperatures so as to avoid possible degradation of the polyphosphoramidite ligand and reaction products.

More particularly, distillation and separation of the desired aldehyde product from the metal-polyphosphoramidite complex catalyst containing reaction fluid may take place at any suitable temperature desired. In general, it is preferred that such distillation take place at relatively low temperatures, such as below 150° C., and more preferably at a temperature in the range of from 50° C. to 140° C. It is also generally preferred that such aldehyde distillation take place under reduced pressure, e.g., a total gas pressure that is substantially lower than the total gas pressure employed during hydroformylation when low boiling aldehydes (e.g., C_4 to C_6) are involved or under vacuum when high boiling aldehydes (e.g. C_7 or greater) are involved. For instance, a common practice is to subject the liquid reaction product medium removed from the hydroformylation reactor to a pressure reduction so as to volatilize a substantial portion of the unreacted gases dissolved in the liquid medium that now contains a much lower synthesis gas concentration than is present in the reaction medium to the distillation zone, e.g. vaporizer/separator, wherein the desired aldehyde product is distilled. In general, distillation pressures ranging from vacuum pressures on up to total gas pressure of 340 kPa should be sufficient for most purposes.

Once catalyst activity has declined to less than desirable levels, the catalyst solution can be rejuvenated using embodiments of the present invention. For example, catalyst activity may be less than desirable when the hydroformylation reaction rate has decreased such that a hydroformylation reactor is not reaching production targets. In general, the catalyst solution can be rejuvenated by the addition of (1) a peroxide solution, followed by, optionally (2) fresh polyphosphoramidite ligand.

In one embodiment the catalyst solution is concentrated prior to the treatment of the invention. This is accomplished by turning off the olefin, carbon monoxide and hydrogen feeds while continuing to maintain process temperatures. The catalyst solution is passed through the vaporizer until the aldehyde product is substantially removed; this determination may be made by monitoring the product rate (e.g. when the rate of aldehyde collection in the product tank is about 5-10% of normal operation). Once the aldehyde product has been removed, the peroxide solution is added to the concentrated catalyst solution at elevated temperature; preferably from 70-110° C., more preferably from 80-100° C.

In some embodiments, the process of the invention may be conducted within the hydroformylation process equipment during suspension of operation, but without pre-concentrating the hydroformylation process fluid. For example, the olefin, carbon monoxide and hydrogen feeds are turned off, the process temperatures lowered, and the peroxide solution is added to the hydroformylation process fluid at near ambient temperature. The resulting catalyst solution-peroxide mixture is circulated or stirred for a period of 1-7 days; more preferably for a period of 2-6 days. Fresh ligand is then added, and process temperatures and gas feeds are reestablished to resume hydroformylation.

The molar equivalents of peroxide should approach or slightly exceed the calculated/estimated molar equivalents of phosphorous; about 0.25 to 1.5 molar equivalents of peroxide per mole of phosphorous; preferably about 0.50 to 1.3 molar equivalents; most preferably about 0.7 to 1.1 molar equivalents.

In some embodiments, the amount of peroxide to be added may be estimated based on the total phosphorous content of the solution. Analytical means for determining phosphorous content are well known to the skilled person, and include Gas Chromatography with nitrogen-phosphorous detectors, (GC-NPD), Atomic Absorption (AA) and X-ray fluorescence (XRF). Due to the ease of operation and lack of need for sample preparation, XRF is preferred. The XRF analysis can be performed directly on the sample without dilution or additional preparation; a semi-quantitative measurement (precision±20%) may be readily obtained without calibration and is sufficient for the procedure of the invention.

While the amount of peroxide to be added is an important aspect, the present invention is tolerant of slight variations, and as such basing the amount of peroxide to be added on the molar concentration of phosphorous is a suitable means of carrying out the invention.

In some embodiments, the amount of peroxide to be added is based on polyphosphoramidite ligand concentration. In commercial hydroformylation processes, the concentration of the ligand employed and many of its associated decomposition products are routinely determined through at least one analytical method, including but not limited to 31P NMR and HPLC. Due to simplicity of operation, HPLC is typically preferred. In such an embodiment, once the concentration of ligand and byproducts are known, a reasonable estimate of the molar concentration of the phosphorous-containing compounds may be made, and an appropriate amount of peroxide added. The post-treatment solution may then be analyzed to confirm the desired decline in phosphorous compound concentration. Based on the post-treatment analytical results, additional peroxide may be added if desired.

While peroxides are known to decompose at elevated temperature, in some embodiments it may be desirable to determine the post-oxidation concentration of peroxide by analysis. Methods for analyzing peroxide content in organic solutions are known and include, but are not limited to peroxide test strips, GC analysis, and titrations. Due to the ease of use, peroxide test strips are preferred.

Following the peroxide treatment, fresh polyphosphoramidite ligand may be added if desired so as to achieve a polyphosphoramidite ligand concentration of 1-10 moles of ligand per mole rhodium; preferably 1-5 moles per rhodium; most preferably 1.2-3 moles per rhodium. Polyphosphoramidite ligand concentration should be determined by HPLC, rhodium content should be determined by atomic absorption (AA), and additional ligand can be added as necessary to maintain the desired concentration.

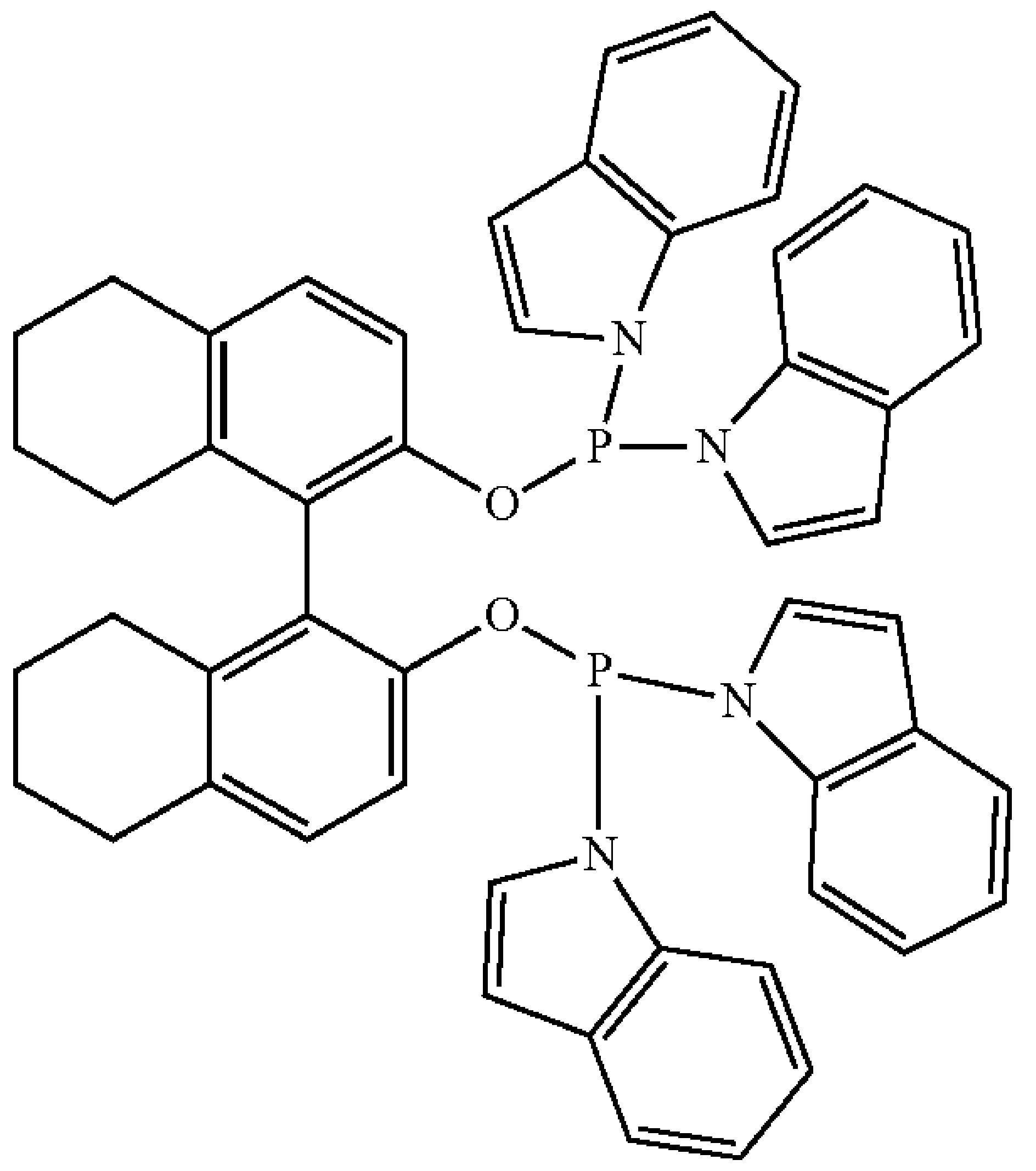
Illustrative non-optically active aldehyde products include e.g., propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, 2-methyl 1-butyraldehyde, hexanal, hydroxyhexanal, 2-methyl 1-heptanal, nonanal, 2-methyl-1-octanal, decanal, adipaldehyde, 2-methylglutaraldehyde, 2-methyladipaldehyde, 3-hydroxypropionaldehyde, 6-hydroxyhexanal, alkenals, e.g., 2-, 3- and 4-pentenal, alkyl 5-formylvalerate, 2-methyl-1-nonanal, 2-methyl 1-decanal, 3-propyl-1-undecanal, pentadecanal, 3-propyl-1-hexadecanal, eicosanal, 2-methyl-1-tricosanal, pentacosanal, 2-methyl-1-tetracosanal, nonacosanal, 2-methyl-1-octacosanal, hentriacontanal, and 2-methyl-1-triacontanal.

Illustrative optically active aldehyde products include (enantiomeric) aldehyde compounds prepared by the asymmetric hydroformylation process of this invention such as, e.g. S-2-(p-isobutylphenyl)-propionaldehyde, S-2-(6-methoxy-2-naphthyl)propionaldehyde, S-2-(3-benzoylphenyl)-propionaldehyde, S-2-(3-fluoro-4-phenyl)phenylpropionaldehyde, S-2-(2-methylacetaldehyde)-5-benzoylthiophene and the like.

Some embodiments of the present invention will now be described in the following Examples.

EXAMPLES

All parts and percentages in the following examples are by weight unless otherwise indicated. Pressures are given as absolute pressure unless otherwise indicated. Solutions of t-butyl hydroperoxide in water (70 wt %) and in nonane (5-6 M) are purchased from Aldrich and used as received. Hydrogen peroxide (30 wt % in water) was purchased from Aldrich and additionally diluted with deionized water. Ligand A is used in these Examples:



Ligand A

General Procedure

Hydroformylation Test Unit description—A liquid recycle reactor system that consists of a 1 liter stainless steel stirred tank reactor equipped with a vertically mounted agitator and a circular tubular sparger located near the bottom of the reactor. The sparger contains a plurality of holes of sufficient size to provide the desired gas flow into the liquid body in the reactor. The sparger is used for feeding the olefin and/or syngas to the reactor, and can also be used to recycle unreacted gases. The reactor has a silicone oil shell as a means of controlling reactor temperature. The reactor also contains a pneumatic liquid level controller for maintaining the desired liquid level and a blow-off vent for removal of unreacted gases. A portion of the liquid reaction solution is continuously pumped to a vaporizer, which consists of a heated vessel at reduced pressure. The effluent stream from the vaporizer is sent to a gas-liquid separator located at the bottom of the vaporizer, where vaporized aldehyde is separated from the non-volatile components of the liquid reaction solution. The vaporized aldehyde product is condensed and collected in a product receiver. A pneumatic liquid level controller controls the desired non-volatile component level, including catalyst to be recycled, at the bottom of the separator.

Glass Reactor description—Hydroformylation Examples and Comparative Experiments are conducted in 90 mL flow-through Fisher Porter reactors equipped with means for accurate control of temperatures and gas flows. Mixing in the flow-through reactor is effected by continuous gas flow via a sparger at the bottom of the reactor. This reactor design is described in detail in U.S. Pat. No. 5,731,472, the teachings of which are incorporated by reference. Hydroformylation conditions are 100 psi 1:1 syn gas, 10 psi propylene, 150 psig total pressure (balance nitrogen) at 100° C. unless otherwise indicated. Reactor off gases are analyzed by online GC to determine partial pressures and product selectivity; and to allow calculation of reaction rates using Dalton's Law. Reaction rates are expressed as the moles of aldehyde produced per volume of catalyst solution per unit time (moles/L-hour); this value is additionally divided by the propylene partial pressure to help dampen the effects of small, unavoidable fluctuations in the propylene feed rate (rate/olefin). Product selectivity is expressed as the ratio of linear (normal) aldehyde versus branched (iso) aldehyde (N:I) as well as the percentage of linear aldehyde.

Aliquots of the following deactivated catalyst solution are used for some Examples:

Catalyst solution A—Catalyst solution comprised of rhodium and Ligand A is charged to the Hydroformylation Test Unit and used for the hydroformylation of propylene under varying conditions for a period of time. During the course of the run the hydroformylation rate demonstrated by the catalyst declines to approximately 40% of a fresh rhodium-Ligand A catalyst under comparable concentrations and reaction conditions. Phosphorous content is estimated based on HPLC analyses (0.0025M).

Catalyst solution B—Catalyst solution comprised of rhodium and Ligand A is charged to the Hydroformylation Test Unit and used for the hydroformylation of propylene under varying conditions for a period of time. During the course of the run the hydroformylation rate demonstrated by the catalyst declines to approximately 50% of a fresh rhodium-Ligand A catalyst under comparable concentrations and reaction conditions. Phosphorous content is determined by XRF (0.0038M).

Peroxide concentration is expressed as the molar concentration in the catalyst solution.

Comparative Experiment A

Tetraglyme (20 mL) is added to a Glass Reactor and placed under flowing syn gas. Stock solutions of rhodium (185 ppm final concentration) and ligand A (2.0 equivalents of Ligand A per rhodium) in toluene are added. Hydroformylation is initiated and performance for this fresh catalyst is determined (0.4559 rate/olefin; N: I=51; 98.07% linear aldehyde).

Comparative Experiment B

Catalyst Solution A (30 mL) is added to a Glass Reactor, and the excess butyraldehyde is stripped off at 100° C. under flowing syn gas overnight. Tetraglyme (10 mL) is then added to give a final volume of 20 mL (final rhodium concentration is 185 ppm). A solution of Ligand A in toluene is added (2.0 equivalents of Ligand A per rhodium), flows of carbon monoxide, hydrogen and propylene are established and catalyst performance is determined.

Example 1

Catalyst solution A (30 mL) is added to a Glass Reactor, and the excess butyraldehyde is stripped off at 100° C. under flowing 1:1 syn gas overnight. Tetraglyme (10 mL) is then added to give a final volume of about 20 mL (final rhodium concentration is 185 ppm). A solution of t-butyl hydroperoxide (70% in water) is added (0.13 mL; 0.054M final concentration); no color change or sign of reaction is observed. After about 30 minutes, a solution of Ligand A in toluene is added (2.0 moles of Ligand A/mole rhodium) and hydroformylation is initiated 30 minutes later.

Example 2

The procedure of Example 1 is repeated, with the exception of the amount of t-butyl hydroperoxide solution that is added (0.20 mL; 0.095M final concentration). A change in color from yellow to orange is noted.

The results of Comparative Experiment B and Examples 1 and 2 are shown in Table 1.

TABLE 1

Summary of catalyst performance for Comparative Experiment B and Examples 1 and 2.

	Comparative Exp B			Example 1			Example 2		
Days of operation	rate/olefin	N: I	% linear aldehyde	rate/olefin	N: I	% linear aldehyde	rate/olefin	N: I	% linear aldehyde
1	0.1915	51	98.08	0.3918	45	97.83	0.4061	46	97.87
2	0.1835	50	98.04	0.4200	41	97.62	0.4551	42	97.67
3	0.1724	49	98.00	0.3689	32	96.97	0.4767	40	97.56

The results in Table 1 show the ability to restore hydroformylation activity to a previously deactivated catalyst via an embodiment of a process of the invention. The post-treatment reaction rates are near to (Example 1) and comparable to (Example 2) that of a fresh catalyst (Comparative Experiment A). The selectivity to linear aldehyde for the treated solution is slightly lower, but still comparable to a fresh catalyst (Comparative Experiment A; 98% linear aldehyde).

Comparative Experiment C

The procedure of Comparative Experiment B is repeated, with the exception of concentrating the catalyst solution under flowing syn gas for 3 hours.

Example 3

The procedure of Example 2 is repeated, with the exception of concentrating the catalyst solution under flowing syn gas for 3 hours, and the use of t-butylhydroperoxide in nonane (5-6M solution; 0.054 M final concentration).

Example 4

The procedure of Example 3 is repeated, with the exception of the amount of t-butylhydroperoxide in nonane used (5-6M solution; 0.095 M final concentration).

The results of Comparative Experiment C and Examples 3 and 4 are shown in Table 2.

TABLE 2

Summary of catalyst performance for Comparative Experiment C and Examples 3 and 4.

	Comparative Exp C			Example 3			Example 4		
Days of operation	rate/olefin	N: I	% linear aldehyde	rate/olefin	N: I	% linear aldehyde	rate/olefin	N: I	% linear aldehyde
1	0.1562	55	98.21	0.2534	53	98.15	0.2985	50	98.04
2	0.1537	53	98.15	0.3055	47	97.92	0.3422	47	97.92
3	0.1530	55	98.21	0.3309	46	97.87	0.3635	45	97.83

The results shown in Table 2 demonstrate the ability to double the reaction rate of a deactivated rhodium-polyphosphoramidite catalyst using an embodiment of process of the invention.

Comparative Experiment D

The procedure of Example 3 is repeated with the exception of the amount of peroxide added (0.156M final concentration).

Comparative Experiment E

The procedure of Example 3 is repeated with the exception of the amount of peroxide added (0.195 M final concentration).

The results of Comparative Experiment C, D and E are shown in Table 3.

TABLE 3

Summary of catalyst performance for Comparative Experiment C, D and E.

	Comparative Exp C			Comparative Exp D			Comparative Exp E		
Days of operation	rate/olefin	N: I	% linear aldehyde	rate/olefin	N: I	% linear aldehyde	rate/olefin	N: I	% linear aldehyde
1	0.1562	55	98.21	0.2601	35	97.22	0.1853	31	96.88
2	0.1537	53	98.15	0.1838	30	96.77	0.1320	28	96.55

The results of Table 3 show that unsatisfactory results are achieved when the amount of peroxide is further increased above the levels in Examples 3 and 4.

Example 5

Catalyst solution B (20 mL) is added to a Glass Reactor along with Tetraglyme (10 mL) and the excess butyraldehyde is stripped off at 100° C. under flowing 1:1 syn gas overnight to give a final volume of about 16 mL (final rhodium concentration is about 120 ppm). A solution of hydrogen peroxide (3% in water) is added (1.0 mL; 0.060 M final concentration). After about 5 minutes a change in solution color is noted (clear yellow to clear pale orange). After 15 minutes a solution of Ligand A in toluene is added (2.0 moles of Ligand A/mole rhodium) and hydroformylation is initiated.

Comparative Experiment F

The procedure of Example 5 is repeated with the exception of no peroxide or ligand being added.

The results of Example 5 and Comparative Experiment F are summarized in Table 4.

TABLE 4

Summary of Comparative Experiment F and Example 5

	Comparative Exp F			Example 5		
Days of operation	rate/olefin	N: I	% linear aldehyde	rate/olefin	N: I	% linear aldehyde
1	0.1041	40.4	97.52	0.1980	47.9	97.91
2	0.0918	39.7	97.48	0.2029	45.7	97.81

The results of Table 4 show the results of an embodiment of a process of the invention using hydrogen peroxide.

Comparative Experiment G and Example 6-8

Catalyst solution B (20 mL) is added to each of four Glass Reactors along with 10 mL of tetraglyme; the excess butyraldehyde is stripped off at 100° C. under flowing 1:1 syn gas overnight, resulting in a solution volume of about 17 mL and a final rhodium concentration of approximately 185 ppm. Solutions of t-butyl hydroperoxide in water are added to Examples 6-8 (0.20 mL of differing concentrations); 0.20 mL of deionized water is added to Comparative Experiment G. A solution of Ligand A in toluene (1.5 moles Ligand A per mole rhodium) is then added to all reactors and hydroformylation initiated. The resulting catalyst performance is summarized in Table 5.

	Comparative Exp G (0 peroxide)			Example 6 (0.0095M peroxide)			Example 7 (0.0238M peroxide)			Example 8 (0.0475M peroxide)		
Days	rate/ole	N: I	% linear ald	rate/ole	N: I	% linear ald	rate/ole	N: I	% linear ald	rate/ole	N: I	% linear ald
1	0.1159	62.9	98.41	0.1852	60.4	98.34	0.2239	49.6	97.98	0.2432	49.9	98.00
2	0.1020	59.5	98.32	0.1608	56.7	98.24	0.2031	46.2	97.84	0.2300	43.8	97.72

The results of Table 5 show the ability to increase the hydroformylation rate through embodiments of processes of the invention with varying amounts of peroxide.

Taken collectively, the results presented herein demonstrate that the performance of an aged and deactivated hydroformylation catalyst comprised of rhodium, polyphosphoramidite and polyphosphoramidite degradation products can be greatly improved via embodiments of processes of the invention.

What is claimed is:

1. A method to rejuvenate a deactivated hydroformylation catalyst solution comprising rhodium, polyphosphoramidite ligand, and polyphosphoramidite ligand degradation products, the method comprising: adding a peroxide to the deactivated hydroformylation catalyst solution.

2. The method of claim **1**, further comprising adding additional polyphosphoramidite ligand to the catalyst solution after the addition of peroxide.

3. The method of claim **1**, wherein the deactivated hydroformylation catalyst solution is at a temperature of between 0° C. and 40° C. when the peroxide is added.

4. The method of claim **1**, wherein the deactivated hydroformylation catalyst solution further comprises at least one product aldehyde, and further comprising removing a majority of the product aldehyde prior to adding the peroxide.

5. The method of claim **4**, wherein a majority of the product aldehyde is removed by vaporization.

6. The method of claim **4**, wherein the deactivated hydroformylation catalyst solution is at the temperature of 70° C. or greater when the peroxide is added.

7. The method of claim **4**, wherein the deactivated hydroformylation catalyst solution is at the temperature of 100° C. or greater when the peroxide is added.

8. The method of claim **4**, wherein the peroxide comprises hydrogen peroxide, peroxy esters, peroxydicarbonates, dialkyl peroxides, hydroperoxides, peroxyketals, or a combination thereof.

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